Effect of Disorder on the Conduction-Band Effective Mass, Valence-Band Spin-Orbit Splitting, and the Direct Band Gap in III-V Alloys

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The conduction-band effective mass in small-band-gap III-V alloys has been observed to be heavier than would be expected from a standard $\vec{k}\cdot\vec{p}$ calculation in the virtual-crystal approximation. Here we analyze the effect of disorder-induced valence-conduction band mixing on this effective mass. It is found that with a consistent set of assumptions for interband and intraband mixing, one can account for the variation of the band gap, the spin-orbit splitting, and the conduction-band mass in these alloys.

Experimental data on the variation of the energy gap E_0, the spin-orbit splitting Δ_0, and the conduction-band effective mass m_0 as a function of composition are now available for a number of III-V alloy systems[1-14] (see Figs. 1-3). These data thus provide a good test for any proposed theoretical calculations of alloy band structure, since any such analysis should be capable of making predictions concerning all three parameters. In almost all theoretical work on semiconductor alloys, the starting point has been the virtual-crystal approximation[15] (VCA). Essentially, the potential $V(r)$ is considered to be represented by the sum of a periodic term V_p and an aperiodic term V_a.[16,17] The use of the V_p term, or its equivalent, in any standard type of calculation gives the band structure of the virtual crystal. The effect of the aperiodic term due to the disorder of the lattice has then to be included. In some work it has been suggested that the effect of the aperiodic term is small[18,19] and can thus be ignored. However, the present authors have argued that the pronounced downward bowing of Δ_0 as a function of composition in these alloys (Fig. 2) conclusively demonstrates that the disorder effect is of importance and must be included in the analysis.[20,21]

One method of including this effect is by treating the aperiodic term as a perturbation in the VCA solution.[16] However, in some alloy systems, particularly those with small band gap E_0, the aperiodic term would appear to be so large that normal perturbation theory is not valid when the behavior at the Γ point is being considered.[20] Thus, some other approach must be used.

For all III-V systems investigated experimentally, it has been found that the variation of E_0 with composition x is of the form

$$E_0 = a + bx + cx^2 , \tag{1}$$

with the bowing parameter c positive. In an attempt to calculate the variation of E_0 with x, Van Vechten and Bergstresser[17] first used the dielectric model[22] in the VCA to give values E_{0v} (see Fig. 1). The curves of E_{0v} vs x, as obtained, show bowing (described by bowing parameters c_i) but always to a lesser degree than that found experimentally (i.e., $c_i < c$). The difference $E_{0v} - E_0 = \delta E(x)$ has been attributed to the effects of the aperiodic potential term due to the disorder. It was shown that to a good approximation for all systems investigated, δE can be expressed as

$$\delta E = x(1-x)C_{FG}^2/A , \tag{2}$$

where C_{FG} is the Phillips electronegativity difference[23] between the mixed elements and A is a constant bandwidth parameter, found by comparison with experiment to be 1.0 eV for all alloy systems. At this stage the detail of the effect of disorder was not discussed.

Turning to the values of spin-orbit splitting, experimental data are available for both Δ_0, the valence-band splitting at the Γ point, and Δ_1, the splitting at the L point, as a function of x[8,13,14] (see Fig. 2). It is found that in all cases, the $\Delta_1(x)$ curve is bowed upwards (negative c) while the $\Delta_0(x)$ curve bowed downwards (positive c). In the VCA, $\Delta_0(x)$ and $\Delta_1(x)$ deviate from linearity only to the extent that the overlap of the relevant wave functions with the nuclei vary,[24] which is very little. Thus, the signs and magnitude of the bowing of $\Delta_0(x)$ and $\Delta_1(x)$ must be explained by the aperiodic effects. The present authors[20] have indicated that the $\Delta_1(x)$ behavior can be explained in terms of a simple perturbation of the VCA results, but that to explain the variation of Δ_0 with x some further effect must be postulated. It has been suggested[20] that, because of the breaking of the crystal symmetry by the aperiodic terms, mixing of the valence- and conduction-band states occurs at the Γ point. If we denote by $y(x)$ the fraction of conduction-band

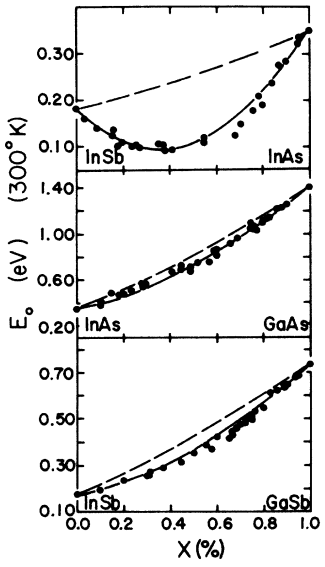

FIG. 1. Variation of E_0 with composition x for various alloy systems: •, experimental data (Refs. 2, 3, 7, 26, 27); - - -, virtual-crystal values; —, theoretical curves including effects of aperiodicity (Ref. 17).

s character mixed into the valence band at Γ, then this s-like component makes zero contribution to Δ_0, so the splitting at Γ is reduced by a factor of $(1-y)$. From comparison with the effect of disorder on E_0, y is assumed to have the form

$$y = \frac{x(1-x)C_{FG}^2}{A\tilde{E}_{0v}} ,$$

where

$$\frac{3}{\tilde{E}_{0v}} = \frac{2}{E_{0v}} + \frac{1}{(E_{0v}+\Delta_{0v})} . \tag{3}$$

Values of Δ_0 thus calculated, were found to show reasonable agreement with the experimental values (see Fig. 2).

When room-temperature values of m_0, the bottom of the conduction-band effective mass, were determined for $InAs_xSb_{1-x}$[9] and $Ga_xIn_{1-x}Sb$[10] alloy systems, it was assumed that a Kane model[25] applied in these cases and values of the square of the matrix element, P^2, were calculated. It was found that although the values of P^2 varied little from one compound to another, the values determined in this way for the alloys showed a minimum at the center of the alloy range.[9] Recently, Fetterman *et al.*[12] determined m_0 for a limited range of $Ga_xIn_{1-x}As$ alloys. Assuming that P^2 varied linearly between the values for the compounds, they showed that the values calculated from a simple Kane model did not agree with the experimental values. This is essentially the same conclusion as found above for $InAs_xSb_{1-x}$ and $Ga_xIn_{1-x}Sb$. (Values of m_0 have been obtained by four types of experiments: Faraday

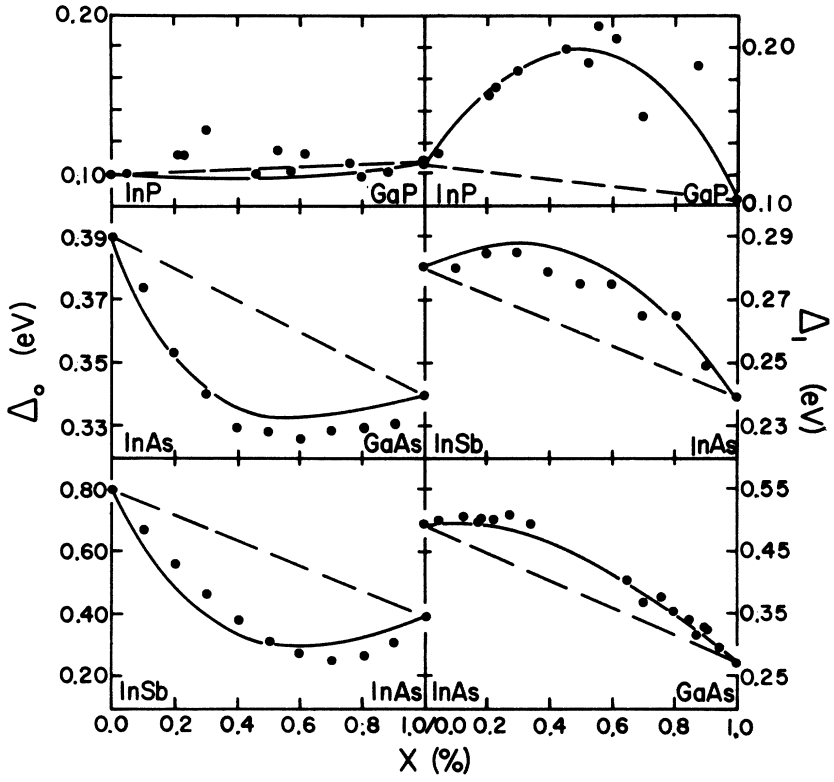

FIG. 2. Variation of spin–orbit splittings Δ_0 and Δ_1 with composition x for various alloy systems: •, experimental data (Refs. 8, 13, 13); - - -, virtual-crystal values; —, theoretical curves including effects of aperiodicity (Ref. 20).

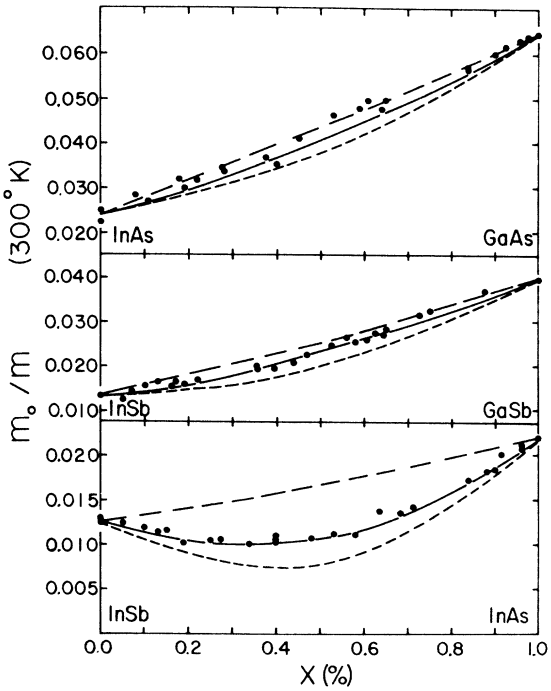

FIG. 3. Variation of electron effective mass at Γ_{1c} with composition x for various alloy systems: (a) ●, experimental data (Refs. 9–12, 28); (b) — — —, virtual-crystal values, (c) - - -, Kane-model values; (d) —, values from present analysis including interband effects.

rotation, magnetothermoelectric power, infrared reflectance, and cyclotron resonance. There is no detectable difference among the values obtained by these different types of experiments.[10] Therefore, we conclude that the discrepancy between experiment and the simple Kane model is not due to any systematic experimental error.) It is now suggested that this deviation from a simple Kane model form is due to the same conduction–valence-band mixing which was required to explain[20] $\Delta_0(x)$.

When such band mixing occurs, the fraction of valence-band states transferred to the conduction band equals the fraction of conduction-band states transferred to the valence band. Hence, the resultant conduction-band effective mass will be determined to some extent by valence-band values. Let y_1, y_2, and y_3 be the fractions of heavy-hole, light-hole, and split-off valence-band states mixed into the conduction band. To be consistent with Eq. (3), it is assumed that

$$y_1 = y_2 = \frac{x(1-x)C_{FG}^2}{3AE_{0v}}\,, \qquad y_3 = \frac{x(1-x)C_{FG}^2}{3A(E_{0v}+\Delta_{0v})}\,. \tag{4}$$

The resultant conduction-band effective mass can be written

$$\frac{1}{m_0} = \frac{(1-2y_1-y_3)}{m_{c0}} + \frac{y_1}{m_{hh}} + \frac{y_1}{m_{lh}} + \frac{y_3}{m_{so}}\,, \tag{5}$$

where m_{c0}, m_{hh}, m_{lh}, and m_{so} are the values the various effective masses would have in the absence of conduction–valence-band mixing,

$$\frac{1}{m_0} = \frac{1}{m_{c0}} + \frac{x(1-x)C_{FG}^2}{3A}\left[\frac{1}{m_{hh}E_{0v}} + \frac{1}{m_{lh}E_{0v}} + \frac{1}{m_{so}(E_{0v}+\Delta_{0v})} - \frac{1}{m_{c0}}\left(\frac{2}{E_{0v}} + \frac{1}{(E_{0v}+\Delta_{0v})}\right)\right]. \tag{6}$$

In order to determine $m_0(x)$ for any system, the parameters in Eq. (6) need to be known. Here, the following assumptions have been made. E_{0v} and Δ_{0v} are the VCA values and are obtained from the Van Vechten and Bergstresser analysis, i.e., E_{0v} is calculated from the values of c_i given by Van Vechten and Bergstresser and Δ_{0v} is assumed linear with x. Similarly m_{hh} and m_{so} are assumed to vary linearly between the values for the compounds. The light-hole mass m_{lh} has been assumed to have the same value as m_{c0}, which is a good approximation in the Kane model. Finally, m_{c0} is the effective mass for the conduction band in the absence of conduction–valence-band mixing but with all other effects, in particular the true $E_0(x)$, included. Thus, it has been assumed that m_{c0} is given by the simple Kane-type equation,

$$\frac{m}{m_{c0}(x)} = 1 + \frac{P^2}{3}\left(\frac{2}{E_0} + \frac{1}{E_0+\Delta_0}\right), \tag{7}$$

where P^2 is linearly interpolated between the values for the compounds and E_0 and Δ_0 take the experimentally observed values. (Note that P^2 will not be affected by interband mixing if this occurs with a random phase.)

The experimentally observed $m_0(x)$ for the three alloy systems $InAs_xSb_{1-x}$, $Ga_xIn_{1-x}As$,[11] and $Ga_xIn_{1-x}Sb$[10] are shown in Fig. 3 [curve (a)]. Also shown in each case are the following curves: (b) The VCA prediction m_{vc} obtained by using the values E_{0v} and Δ_{0v} in Eq. (7); (c) the simple Kane model prediction m_{c0} obtained by substituting the measured values of E_0 and Δ_0 into Eq. (7) and assuming P^2 varies linearly; (d) our prediction m_0 obtained from Eq. (6).

Although the agreement is not perfect, it is seen that the values obtained by assuming conduction–valence-band mixing give the best fit to the experimental values. Thus, it may be concluded that conduction–valence-band mixing is present and must be taken into account in calculating effective-mass values and other band parameters. The conduction band in alloy semiconductors will not be accurately represented by a Kane-type equation if the VCA is assumed.

This latter conclusion raises the question of the

accuracy of the experimentally determined value of m_0. In almost all cases, the experimental observations have been made on n-type material and the results then compared to give a bottom of the band value. This correction has been made using a Kane model. However, in the majority of the results quoted here, the doping of the samples was not large so that the Fermi level was normally within 1 or 2 $k_B T$ (at room temperature) of the band edge and hence the correction term was relatively small. Thus, the error in assuming a simple Kane model is an error in this correction term only and should not be too large a percentage of the quoted final value. However, this effect might explain some discrepancy between experimental and predicted values of m_0.

It is of interest to consider qualitatively the effects which cause the observed changes in the values of E_0, Δ_0, or m_0. The presence of disorder, which breaks the symmetry of the lattice, produces interactions between various states in the Brillouin zone. The ones of interest here can be considered under two headings: (i) intraband interactions as discussed by Parmenter[16] and (ii) interband interactions as proposed by the present authors.[20] Both of these will affect the band energies at the Γ point. Intraband effects in the conduction band will push the minimum of that band to lower energies and, similarly, in the valence band will increase the energy of the maximum; this leads to a reduction of E_0. According to simple perturbation theory, conduction-band–valence-band mixing will cause the bands to separate, leading to an increase in E_0. It seems clear that the intraband effects on E_0 are larger since $E_0(x)$ is less than the VCA prediction (see Fig. 1).

In the case of $\Delta_0(x)$, the problem is more complicated since interactions between valence bands will occur. Intraband effects will raise the energy of both the degenerate valence bands and the split-off valence band so the effect on Δ_0 may be small. Inter-valence-band interaction will tend to separate the interacting bands and hence would increase Δ_0. However, this effect, which causes the observed increase in Δ_1 with disorder [giving the upward curvature of the $\Delta_1(x)$ curve], is relatively small for Δ_1 for the cases of interest here, for which both Δ_1 and Δ_0 are large.[20] As this effect is inversely proportional to the splitting, and as $\Delta_0 \approx 1.5\,\Delta_1$, it should be still smaller for Δ_0. The sum of the intraband effects and inter-valence-band effects at the Γ point would thus be small and in the previous work[20] on Δ_0 it was treated as negligible. Hence, the major disorder effect on Δ_0 is the conduction–valence-band interaction which results in mixing of s-like states into the valence band. As has been shown previously, the form of the $\Delta_0(x)$ curve can be well explained on this basis.

Finally, in the case of the variation of $m_0(x)$, the effects of the various interactions can again be seen; the results for $InAs_xSb_{1-x}$ alloys show these particularly well. As indicated above, the various interactions will cause a reduction in E_0 and this of itself would produce a corresponding reduction in m_0. Thus, the effects of intraband interactions can, to a good approximation, be taken into account by using a Kane equation and the experimentally observed values of E_0 and Δ_0 to calculate values for m_{c0}. The change in effective mass due to this effect, i.e., from m_{vc} to m_{c0}, is in fact the difference between curves (b) and (c) in Fig. 3. In addition, however, the conduction–valence-band mixing causes transfer of valence-band states to the conduction band thus increasing the effective mass in the band. This increase is the difference between curve (c) and the final curve (d) in Fig. 3. It is seen that the reduction from curve (b) to (c) is larger than the increase from (c) to (d), again indicating that intraband interactions have the largest effect, consistent with the results for E_0.

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[21]As noted in Ref. 20, the only real motivation for hypothesizing that V_a is negligibly small in substitutional alloys has been that the band edges observed in the optical spectra of these materials are essentially as sharp as in the pure compounds. [See P. J. Dean, G. Kaminsky, and R. B. Zetterstrom, Phys. Rev. **181,** 1149 (1969).] On the basis of a simple theory, such as that of Ref. 16, which presumes the atoms to be situated on the sites of a perfect virtual lattice, one would expect to see pronounced density-of-states tails on the optical gaps, such as are widely discussed and sometimes observed for glasses and amorphous phases, if V_a is significant. However, the atoms are not on the sites of a perfect virtual lattice but have adjusted their positions during annealing to achieve a (local) minimum for the energy of the material [J. C. Woolley, in *Compound Semiconductors*, edited by R. K. Willardson and H. L. Goering (Reinhold, New York, 1962), p. 5]. From thermodynamic considerations, it can be shown that this relaxation of atomic positions will produce sharp band edges, similar to those in the compounds [J. A. Van Vechten, Solid State Commun. **11,** 7 (1972)].

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